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HIGH-CARBON BINDERS IN REFRACTORIES AND CORROSION-RESISTANT CERAMICS TECHNOLOGY (A Review)

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The authors review the literature sources and patents of foreign companies in the field of application of high-carbon organic binders for refractories, composites and technical ceramics. The review reveals the advantages of the new generation of binders with improved properties and describes binders meeting contemporary environmental requirements and not containing free phenol and other carcinogenic and toxic components.

Binders play a crucial role in production of refractories, fireproof composites, and corrosion-resistant ceramics (electrodes, vessels, pipes) in the Al – Mg – Ca – O – Si – C system. The expansion of the product range and the increase in the volume of refractory ceramic production are stimulating extensive development of efficient binders and their active implementation. Foreign manufacturers [1] center their attention on developing highly advanced and environmentally safe binders for refractories and engineering ceramics.

The nature of high-carbon binders, as well as fillers, is the most important factor affecting the quality of ceramic and refractory products. The binder undergoes deep physicochemical modifications in the course of curing and firing, and nevertheless, unlike the traditional temporary technological binder, it remains a part of the end material (product or lining) in modified (coked) form. Approximately half of the binder is removed in firing, and fired samples contain 15 – 20% coked binder [2]. Organic binders with a high coke residue are the most valuable [2, 3], since carbon diminishes penetration of slag and serves to increase the heat-resistance of the articles [4]. Therefore, a high-carbon binder to a great extent predetermines the technical properties of a product, its manufacturing technology, and operating conditions. In this context, the homogeneity of composition and storage and transport stability of a binder are of special importance. As indicated by Table 1, not all technologically efficient binders have a high coke residue.

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The main requirements imposed on binders used in production of carbon-containing refractory materials and linings are the following:

- environmental safety;
- high carbon content of the binder and substantial coke residue (at least 40%);
- storage stability;
- good flow characteristics and adhesion to mineral filler particles providing a high degree of homogeneity during mixture preparation and molding;
- accessibility and reasonable price.

Until recently, the most common binder in production of dolomite and periclase products was coal pitch whose assets include a high content of residual coked carbon and a low price [2, 9]. The cost of refractories based on a coal pitch binder is usually 10 – 20% low those based on a synthetic binder.

However, the yield of coke residue cannot be the only criterion in selecting a binder. Indeed, coal pitch is a blend of indefinite chemical composition containing a substantial amount of polycyclic aromatic hydrocarbons of carcinogenic nature [7]. On thermal decomposition, pitch produces 1,2-benzopyrene, benzoanthracene, perylene, alkylbrazan, etc. [10 – 12]. It is possible to reduce the benzopyrene content nearly to one-tenth using high-temperature treatment of refractories based on a pitch binder, but the substantial investments and power consumption required in that case offset the effect of the low cost of the products. The use of coal pitch necessarily implies coking firing that involves numerous manual labor operations in hard working conditions. Due

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to all of these factors, manufacturers of carbon ceramics and refractories have abandoned pitch-based binders.

The binders generally used in production of periclase articles are based on lignosulfonates obtained in the wood pulp and paper industry by refining of sulfite lye [13]. Lignosulfonates are high-molecular compounds consisting of aromatic nuclei linked by propane residues in non-polar chains with inclusions of polar carbonyl, carboxyl, sulfo-, and hydroxide groups. The presence of certain functional groups determines the specific properties of lignosulfonates [10, 14]. Lignosulfonates exhibit high surface-active parameters, good binding capacity, and are sufficiently common products, although they have low coke residue and contain ammonium that is displaced in reaction with magnesium oxide, which is undesirable regarding environmental safety [14].

The concentrates of sulfite-alcohol distillery residues that were used in production of refractories prior to lignosulfonates are currently not produced by the domestic pulp-and-paper industry, although they have better a binding power than lignosulfonates. However, foreign producers continue to develop binders with improved properties based on these concentrates (USA patent 3923532).

A significant quality factor of carbon-containing products is their strength at temperatures above 1000°C. Experts from Refratechnik (Germany) supply convincing data on the superiority of materials based on polymeric binders within the temperature range of 1000 – 1500°C (Fig. 1) [3].

At present, the materials predominantly used abroad are synthetic resins, above all, furan and phenol resins belonging to an extensive group of thermosetting synthetic resins: melamine, resorcin, carbamide, epoxy, unsaturated polyester, and other resins [15].

The common features of phenol formaldehyde and furan resins include a high degree of polymerization, three-dimensional structure of the carbon skeleton providing for heat resistance, high coke residue, possibility of application both in the liquid and the solid state, as well as lower power consumption than required in production of coal tar.

It is known that the reaction between phenol and formaldehyde depending on the conditions generates different varieties of phenol-formaldehyde resin: novolacs or resols. The former are solid compounds with a softening point of 70 – 110°C, the latter exist in the liquid or solid form with a softening point of up to 70°C. In production of refractories abroad, both varieties are used in the following forms:

– resin of novolac type in solid form or in solution;

– powder of novolac type resin mixed with urotropine;

– resin of resol type as aqueous solution or dissolved in another solvent.

Novolacs are meltable and soluble in organic solvents. They are supplied as lumps or granules when in solid form. Solvents most commonly used for phenol resins of the novolac type are univalent and multivalent alcohols and esters. When employing phenol solution as a binder, a curing agent is added at the end of the mixing process, such as uritropine (hexamethylene tetramine) or paraformaldehyde. The addition of these compounds results in formation of cross links, and curing starts at temperature of 110 – 120°C, where the curing rate is dependent on the temperature. Mixtures of phenol novolac with hexamethylene tetramine are distinguished by the fact that the latter is present in the powder from the beginning in the amount of 5 – 15% and, the same as the temperature, determines the resin curing rate [15].

Extensive use of phenol-formaldehyde resins (PFR) as binders in ceramic technology is due to the following facts:

– adhesion to both oxide and oxygen-free fillers and the good flow parameters of composites based on PFR;

– curing of raw material at relatively low temperatures in a short time;

– thermosetting of PFR (resin in a refractory batch is cured and partly pyrolyzed at about 350°C, therefore complete pyrolysis results in significant power savings in production of refractories);

– sufficient strength of lining based on phenol-formaldehyde resin;

– heat resistance of refractory products based on PFR facilitated by the three-dimensional structure of the polymer formed after resin curing through polycondensation of oligomers;

– the strong carbon skeleton of PFR after heat treatment, with high residual carbon content, which determines the most significant service properties of refractories, i.e. resistance to slag and metal.

– products based on phenol-formaldehyde binder do not undergo a clearly expressed plastic phase, therefore they keep their shape well.

Another advantage of phenol and furan resins is the increase in the strength of refractories in the course of resin carbonization due to their lattice structure [15]. This is a distinction of PFR from other carbon binders, such as coal pitch. PFR have relatively high coke residue, which is supported by thermogravimetric measurements [5, 7]. However, PFR represent such a serious environmental threat that international and Russian environmental authorities call for the exclusion of PFR from production technologies. The most dangerous component of this binder is free phenol. Industry using phenol resins is noted for increased toxicity and the explosion hazard [10]. Nevertheless, replacement of PFR with an equally efficient binder is a difficult problem, since PFR surpasses many industrially produced polymers in physicochemical parameters and efficiency.

The free phenol content is of the utmost importance when selecting a phenol resin of the resol type. The resin previously used contained 20 – 25% free phenol, which did not meet the requirements of EU legislation specifying that the phenol content should not exceed 5%. In this connection, new resins meeting the required specifications were developed abroad.

German scientists developed a phenol resol characterized as an environmentally safe material with high adhesion to filler components, sufficient storage stability of the prepared mixture, and maximum strength after hardening and coking

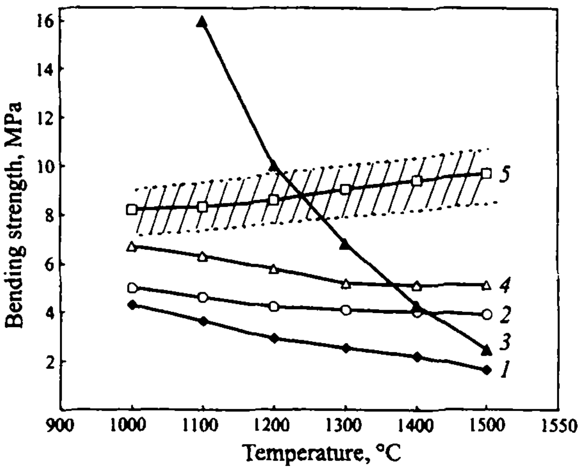

Fig. 1. Variation in bending strength of magnesium-carbon materials depending on temperature: *1*) coal tar binder; *2*) binder based on polymeric thermosetting resin; *3*) coal tar impregnation; *4*) binder and impregnation based on coal tar; *5*) modified polymeric binder.

[3]. The authors note that the concentration of toxic substances in production can be reduced significantly if cold mixing technology is applied. By using phenol resol and thermal polycondensation, one can do without urotropine and organic solvents. Moreover, this binder does not release benzopyrene in the course of decomposition.

Anhydrous phenol resins of the resol type developed by Bakelite GmbH (Germany) are widely used in production of non-fired refractories and fireproof composites. They do not contain polycyclic hydrocarbons, and their content of free phenol and formaldehyde is below 1% [16].

TABLE 1

Binder	Coke residue,%	Reference
Polysiloxane resin	54.5	[5]
Phenol-formaldehyde resin	40 – 60	[6]
Coal pitch	45 – 55	[6]
Furfural resin	45 – 50	[6]
Polyacrylonitrile	44.3	[7]
Phenol-benzaldehyde resin	37.3	[7]
Bitumen	15 – 50	[6]
Coumarone resin	10 – 30	[6]
Carboxymethyl cellulose	15	[8]
Cellulose acetate (LL-1)	11,7	[7]
Lignosulfonate solution (50%)	10	[6]
Melamine resin	10	[6]
Urea-formaldehyde resin (Siakor 151)	8,2	[7]
Polyacrylamide	5.6	[7]
Polyvinyl acetate	4.7	[7]
Ethylcellulose (N-300)	4.5	[7]
Polystyrene	3	[6]
Epoxy resin (Epon 1009)	2.6	[7]
Polyvinyl butyryl (Bakelite XYAL)	1.6	[7]

Powdered phenol resins and novolac resin solutions obtained according to advanced technologies practically do not contain free phenol and are considered to be environmentally safe [17]. However, the appearance of these resins on the market brought about certain modifications in the technology of non-fired products due to some specific properties of the binders caused by the kinetics of their thermal decomposition. Application of the new type of binders requires reconstruction of production technology and using heating equipment designed for a temperature of 800°C, since thermal disintegration of these binders begins at temperatures above 300°C and ends at 800°C with release of the paraffin series compounds that form the polymeric carbon skeleton binding the matrix structure.

Furan resins are pure or mixed liquid polymers based on furfuryl alcohol (furfural). In thermosetting and binding capacities, this type of resin is close to phenol resins. In the process of resin curing at temperatures above 300°C, a three-dimensional carbon skeleton with a sufficiently high carbon residue is formed. The advantage of furan resins is that they are produced from vegetable materials, while phenol resins are based on products of oil and coal processing. Yet, in spite of that, furan resins did not receive wide acceptance in production of refractories abroad.

Foreign producers are developing binders based on resins containing no carcinogenic aromatic hydrocarbons and halogens. Another area for improving the environmental safety of refractory production is the development and implementation of organic binders containing absolutely no phenol. Application of such binders makes it possible to solve simultaneously the problem of increasing the hydratation resistance of the product, improving the mixture moldability, and in some cases increasing the operating characteristics of the product.

The experience in industrial application of natural resins is widely known, but resins of that type used in the 60 – 70s contained aromatic heterocyclic compounds (benzene, toluene, xylene, phenol, cresol, benzopyrene, pyridine), as well as heterocycles containing nitrogen or sulfur. Zimmer and Schwartz GmbH (Germany) developed a complex binder based on a natural resin with additives of hydrocarbons of the paraffin and polyethylene series, fatty acids, and an inorganic binder (German patent 3743217). This technology provides for efficient coating of the filler grains with the binder and produces a hydrophobic effect which makes it possible to achieve a hydratation resistance level of up to 1 month without impregnation of the product.

An organic binder which is an amorphous plastic polymer of a new type with a silicon-carbon bond and improved heat resistance was developed in Japan. The polymer has a lattice structure, softening temperature above 300°C, and is soluble in xylene, hexane, and some other organic solvents. The binder has proved to be successful in refractories, including those of basic composition [18].

British researchers suggest a method for production of carbon-containing refractories in which the binder is a blend

of polymers formed by homopolymerization of resorcinol and isomers of dihydroxydiphenyl and trihydroxydiphenyl. The binder is a thermoplastic mixture with a softening temperature around 80°C and is cured at 300°C. This polymer is environmentally safe and is used for production of refractories based on chamotte, dolomite, corundum, periclase, silicon carbide and others, which exhibit good service properties (Great Britain patent application 2096985A).

There are new safe binders with a high coke residue available, including a thermosetting resin with cyclohexane or acetophenone as solvent, a phenol resin modified with a cyclic compound of alkyl ether or alkylbenzene with a solvent based on ketone ether, a mixture of phenol resin of the resol type with diethyl phtalate or furfural (Japan patent applications 62-109, 63-50304, 62-22943, 1131078, 3-72592).

An efficient complex binder based on carbomethoxy-substituted oligophenyl, synthetic resin, and amine compound which ensures the high strength of heat-treated articles in service has been developed (German patent application 3620473). There are compositions with improved properties based on coal pitch and natural resins, such as a mixture of coal pitch and tar resin (Netherlands patent 182798).

The new technologies for application of polymer resins largely determine the contemporary level of technical progress in production of refractories, corrosion-resistant ceramics, and composites. A special place belongs to thermosetting materials that do not contain phenol and do not release toxic agents in the course of their decomposition, and moreover the articles based on them have good operating characteristics. The development of materials based on combined oligomers makes it possible to reduce the consumption of materials in short supply, improve product quality, and improve the environmental conditions in production of engineering ceramics, refractories, including non-fired refractories, and fireproof polymer-ceramic composite materials.

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